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(54) Title: POLYURETHANE COMPOSITIONS FOR LAMINATING INKS

(57) Abstract: A polyurethane resin is produced by reacting a polymeric diol such as a polyether diol, polyester diol, or mixtures thereof with a diisocyanate to form an isocyanate-terminated prepolymer. The prepolymer is then reacted with a diamine and can be followed by reaction with another amine or an alcohol. Clear solutions of the polyurethane resin are useful in formulating printing ink compositions, adhesives, and clear varnishes.

WO 01/14442 A1

**POLYURETHANE COMPOSITIONS
FOR LAMINATING INKS**

5

BACKGROUND OF THE INVENTION

(1). Field of the Invention

This invention relates to a polyurethane resin, its preparation, an ink
10 composition, in particular, a flexographic packaging printing ink, containing the resin
and a laminate prepared with the resin.

(2). Description of Related Art

Flexographic packaging printing inks are liquid inks applied by
15 cylinders or plates to a variety of flexible substrates, e.g., plastic film materials such
as cellophane, polypropylene and polyethylene, aluminum foils, nylon, paper, which
in turn, are utilized, *inter alia*, to wrap products such as boxed chocolates, toys,
cookies, cigarettes, meat, etc. Where used between two films, the ink provides both
visual indicia and adhesive properties. In this application, such ink compositions are
20 commonly known as laminating inks.

Flexographic packaging printing inks are typically formulated from a
solvent, a pigment, a resin binder and other additives. In particular, the resin binder is
utilized as a delivery vehicle in printing inks and provides the ink with one or more
useful characteristics such as, for example, pigment wetting, abrasion resistance, gloss
25 and adhesion to the substrate. Various alcohol-soluble polymers have been utilized as
resin binders for printing ink formulations, e.g., polyamides, cellulose, acrylic and
methacrylic esters, and rosin esters. Certain polyurethanes have also been utilized in
printing ink formulations. However, because of inconsistencies in adhesion properties
to different substrates, this particular use of polyurethanes has been limited. For
30 example, while a given polyurethane may exhibit good adhesion to a polyolefin
substrate, that same polyurethane might exhibit poor adhesion to polyesters. Poor
solubility of many polyurethanes in solvents commonly used in flexographic

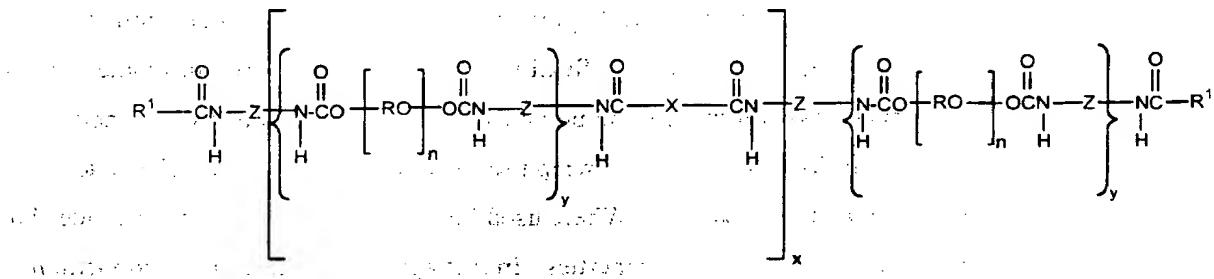
packaging printing inks (e.g., alcohols) also discourages the use of polyurethanes in such inks.

It would be desirable to provide polyurethane compositions which are soluble in the solvents commonly used in flexographic packaging printing inks and which exhibit good adhesion to a variety of substrates. A polyurethane composition 5 exhibiting this combination of properties would be particularly useful as laminating resin binders in printing ink formulations.

SUMMARY OF THE INVENTION

10

In one aspect, a polyurethane resin of the general formula:



15 is provided wherein Z is an aliphatic, cycloaliphatic, aromatic or alkylaromatic group, R is a C₂ to C₈ straight chain or branched hydrocarbon group, the oligomeric reaction product of a C₂ to C₃₆ diol with a C₂ to C₃₆ diacid, or combinations thereof, R' is an amine or alcohol radical, X is the residue of a diamine, n is a number from 1 to 200, x is a number from 1 to 50, and y is a number from 1 to 30, the polyurethane resin being
20 soluble in a solvent containing an aliphatic alcohol to a level of at least 10 weight percent solids.

In another aspect, a method of preparing the foregoing polyurethane resin is provided, which includes a) reacting an excess of an aliphatic, cycloaliphatic, aromatic, or alkylaromatic diisocyanate with a polymeric diol selected from the group consisting one or more polyether diols, one or more polyester diols, and mixtures thereof, to form an isocyanate-terminated prepolymer, b) reacting the prepolymer with

a diamine, and then c) optionally endcapping any free isocyanate groups of the compound formed by step (b) with an amine or alcohol, to form a polyurethane resin which is soluble in a solvent containing an aliphatic alcohol to a level of at least 10 percent by weight solids.

5 The polyurethane resin exhibits desirable properties that render it especially useful in compositions, ink formulations, adhesives and varnishes. In particular, the resin possesses cohesive strength, good alcohol solubility, good viscosity, and blocking resistance which are functions of both molecular and the percentage of hard segments present.

10

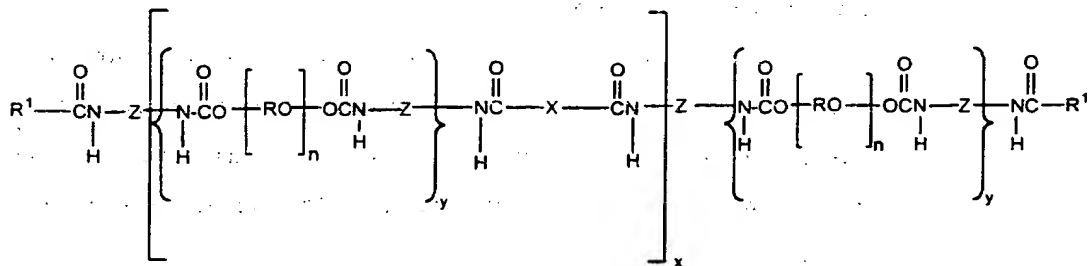
DETAILED DESCRIPTION OF THE INVENTION

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

15 Polyurethane resins are described herein which are useful as binders in formulating printing inks, as adhesives for preparing laminates, and as clear varnishes.

Adhesives typically include a solution of a resin in a solvent, and are useful in binding laminae (layers of substrates) together to form laminates as described in more detail below. Varnishes typically include resins dissolved in oils,
20 alcohol, etc. used to provide a hard, glossy surface to wood, metals and other materials.

In particular, a novel polyurethane resin having the general formula:



25 is provided herein wherein Z is an aliphatic, cycloaliphatic, aromatic or alkylaromatic group, R is a C₂ to C₈ straight chain or branched hydrocarbon group, the oligomeric

reaction product of a C_2 to C_{36} diol with a C_2 to C_{36} diacid, or mixtures thereof, R^1 is an amine or alcohol radical, X is the residue of a diamine, n is a number from 1 to 200, x is a number from 1 to 50, and y is a number from 1 to 30, the polyurethane resin being
5 weight solids. Preferably n is a number from 1 to 70 and x is a number from 1 to 30.

The polyurethane resin is prepared by reacting an aliphatic, cycloaliphatic, aromatic or alkylaromatic diisocyanate with a polymeric diol to provide an isocyanate-terminated polyurethane prepolymer. The prepolymer is then chain extended using a diamine to form urea linkages, and any free-isocyanate groups
10 of the resulting polymer are optionally endcapped with an amine or alcohol to form the polyurethane resin. Typically, the resulting polyurethane resin has a number average molecular weight of from 5,000 to 70,000 and preferably from 15,000 to 40,000.

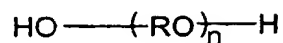
Any diisocyanate of the formula:

15
$$\text{OCN-Z-NCO}$$

wherein Z is an aliphatic, cycloaliphatic, aromatic, or alkylaromatic group can be reacted with a polyether diol, polyester diol, or combinations thereof to prepare the isocyanate-terminated polyurethane prepolymer. Examples of diisocyanates include, but are not limited to, 1,4-diisocyanatobutane, 1,6-diisocyanatohexane, 1,5-
20 diisocyanato-2,2-dimethylpentane, 2,2,4- or 2,4,4-trimethyl-1, 6-diisocyanatohexane, 1,10-diisocyanatodecane, 1,3- and 1,4-diisocyanatocyclohexane, 1-isocyanato-5-isocyanatomethyl-3,3,5-trimethylcyclohexane (isophorone diisocyanate), 2,3- 2,4- and 2,6-diisocyanato-1-methylcyclohexane, 4,4'- and 2,4'-diisocyanatodicyclohexylmethane, 1-isocyanato-3(4)-isocyanatomethyl-1-methyl-
25 cyclohexane, 2,4 and 2,5 and 2,6 tolylene diisocyanate, 1,3 and 1,4 phenylene diisocyanate, 4,4'- and 2,4'-diisocyanatodiphenylmethane, 1,3-bis(1-isocyanato-1-methylethyl)benzene and mixtures thereof. Most preferred is isophorone diisocyanate.

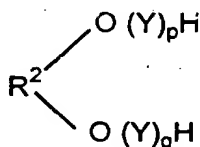
Useful polymeric diols include one or more polyether diols, one or
30 more polyester diols, and mixtures thereof.

Useful polyether diols include those represented by the formula:



wherein R is a C₂ to C₈ straight chain or branched hydrocarbon group. Preferably, R is a C₂ to C₄ alkylene group. Examples of particularly useful polyether diols include, but are not limited to, poly(ethylene ether) glycols, poly(propylene) ether glycols and poly(tetramethylene ether) glycols, with poly(tetramethylene ether) glycols being preferred. The number average molecular weight of the polyether diol typically ranges from 250 to 10,000, preferably from 1000 to 2500, and more preferably from 1250 to 2000. The polyether diols can also contain a minor percentage by weight, e.g., up to about 40 weight percent, of ester units. These diols can be obtained, e.g., by reacting one or more of the aforesaid polyether diols with a lactone such as ε-caprolactone.

Useful polyester diols include those represented by the formula:



wherein R² is the residue of a diol HOR²OH, Y is -OC R³COOR²O in which R² has the aforestated meaning and R³ is the residue of a dicarboxylic acid HOOCR³COOH or anhydride $\text{R}^3\text{C(O)OC(O)}$ thereof, and p and q independently is from about 0 to about 600 and preferably from about 1 to about 100, the sum of p + q being from about 1 to about 1200 and preferably from about 1 to about 250, or Y is -OCR⁴O - in which R⁴ is the residue of a lactone R^4COO or an α, ω - hydroxycarboxylic acid HOR⁴COOH and p, q and the sum of p + q have the aforestated values. Diols HOR²OH, carboxylic acids HOOCR³COOH, anhydrides $\text{R}^3\text{C(O)OC(O)}$, lactones R^4COO and α, ω - hydroxycarboxylic acids HOR⁴COOH that can be used herein include any of those known for preparing polyester diols. Suitable diols include ethylene glycol, propylene glycol, 1, 4-butane diol, neopentyl diol, hexanediol, diethylene glycol, dipropylene glycol, and the like. Suitable dicarboxylic acids and anhydrides include adipic acid,

phthalic acid, phthalic anhydride, and the like. Suitable lactones and α, ω - hydroxycarboxylic acids include butyrolactone, caprolactone, α, ω - hydroxycaproic acid and the like. Examples of particularly useful polyester diols include, but are not limited to, poly(caprolactone) diols, poly(diethylene glycol-co-ortho-phthalic acid),
5 poly(1,6 hexane diol-co-ortho-phthalic acid), poly(neopentyl glycol-co-adipic acid), poly(ethylene glycol-co-adipic acid) and poly(caprolactone) diols. The number average molecular weight of the polyester diol typically ranges from 250 to 10,000, preferably from 500 to 2500, and more preferably from 1000 to 2000. The polyester diols can also contain a minor percentage by weight, e.g., up to about 40 weight
10 percent thereof, of ether units. These diols can be obtained, e.g., by reacting one or more of the aforesaid polyester diols with one or more 1,2-alkylene oxides such as ethylene oxide, propylene oxide, etc.

Polyether diols are desirable in terms of the product polyurethane resin having greater solubility in aliphatic alcohol solvents compared with polyester diols.
15 However, polyester diols impart greater tensile strength to the resin. Therefore, depending on the choice of polymeric diol, the polyurethane resin obtained in accordance with the invention can vary from those resins possessing high solubility and relatively low tensile strength, i.e., those made entirely from polyether diol to those of relatively low solubility and relatively high tensile strength made entirely
20 from polyester diol, and all of the combinations of solubility and tensile strength properties in between as would be the case where mixtures of polyether and polyester diols are employed. Optimum proportion of solubility and strength can be obtained through routine testing.

The polymeric diol and diisocyanate are reacted under conditions
25 which are well known to those skilled in the art. Preferably, the reaction is carried out in the presence of a solvent, which is a solvent that is ultimately used in compositions formulated using the resin such as the solvent system of an ink formulation. Examples of suitable solvents in which the diisocyanate and polymeric diol can be reacted include, but are not limited to alkyl (1-5 carbon) acetates such as methyl
30 acetate, ethyl acetate, propyl acetate, butyl acetate and pentyl acetate, with propyl

acetate being particularly preferred if the resin is to be used in packaging inks or coatings applications.

The total amount of solvent used for preparation of the isocyanate-terminated prepolymer typically ranges from 0 to 90 percent by weight of the total solution, preferably ranges from 10 to 70 percent by weight of the total solution, and more preferably ranges from 25 to 60 percent by weight of the total solution.

A catalyst may be advantageously employed to accelerate the reaction of diisocyanate with diol. Suitable catalysts include, but are not limited to, stannous octylate, stannous oxalate, dibutyltin dilaurate and triethylamine, with dibutyltin dilaurate being preferred.

The ratio of diisocyanate to polymeric diol is chosen to obtain a desired molecular weight as well as a desired level of urethane and urea segments. An excess of diisocyanate is used to ensure that the prepolymer is isocyanate terminated. The equivalent ratio of diisocyanate to diol generally ranges from 1.01 : 1 to 5 : 1, preferably ranges from 1.1 : 1 to 3 : 1, and more preferably ranges from 1.3 : 1 to 2.1 : 1.

Formation of the isocyanate-terminated prepolymer is generally carried out at a temperature ranging from 0 to 130°C, preferably ranging from 50 to 90°C. The time of the reaction generally ranges from a period of from 1 to 12 hours, preferably from 3 to 4 hours.

The isocyanate-terminated prepolymer is then chain extended with a diamine to form a polyurethane resin. The diamine can be any aliphatic, cycloaliphatic, aromatic, or heterocyclic diamine in which each of the amine groups possesses at least one labile hydrogen atom. Among the many suitable diamines are ethylene diamine, 1,2-diaminopropane, 1,3-diaminopropane, hydrazine, diaminobutane, hexamethylene diamine, 1,4-diaminocyclohexane, 3-aminomethyl-3,5,5-trimethylcyclohexylamine (isophorone diamine), 1,3-bis(aminomethyl)cyclohexane, 1,3-bis(aminomethyl)benzene, 2-(aminomethyl)-3,3,5-trimethylcyclopentylamine, bis-(4-aminocyclo-hexyl)-methane, bis-(4-amino-3-methylcyclohexyl)-methane, 1-amino-1-methyl-3(4)-aminomethyl-cyclohexane, bis-(4-amino-3,5-diethylcyclohexyl)-methane, bis-amino-methyl-hexahydro-4,7-

- methanoindane, 2,3-, 2,4- and 2,6-diamino-1-methyl-cyclohexane, dimer diamine (diamine from dimerized fatty acids), norbornane diamine, 2,2,4 and 2,4,4 trimethyl 1,6 hexanediamine, DuPont brand Dytex A and Dytex EB, Huntsman's Jeffamine brand bis(propylamino) polypropylene oxide diamines,
- 5 bis(aminomethyl)tricyclodecane, piperazine, 1,3-di-piperidylpropane, aminoethylpiperazine, with isophorone diamine being preferred.

The conditions under which the diamine is reacted with the prepolymer are not critical and are within the purview of one skilled in the art. Preferably, the reaction is carried out in the solvent or in a component of the solvent system

10 ultimately used in the final composition formulated from the ink resin as described.

The amount of solvent utilized in the chain extension reaction generally ranges from 0 to 90 percent by weight, and preferably from 35 to 60 percent by weight. The ratio of isocyanate end groups of the prepolymer to amines from the diamine monomer determines the final polymer molecular weight of the resin as well as the level of urea

15 groups. Generally the mole ratio of diisocyanate to diamine is from 6:1 to 1:5, preferably from 4:1 to 1:4. Typically, when the prepolymer is reacted with a stoichiometric excess of the diamine, no residual unreacted isocyanate groups remain in the prepolymer. Accordingly, reaction of the chain-extended prepolymer with an amine or alcohol terminating agent to endcap unreacted isocyanate groups on the

20 chain-extended prepolymer is not required. Alternatively, if less than a stoichiometric excess of diamine is utilized, unreacted isocyanate groups may be present which can be endcapped as described below. The chain extension reaction with diamine is generally carried out at a temperature ranging from 0 to 90°C, and preferably ranging from 25 to 75°C.

- 25 Following the chain extension reaction with diamine, if unreacted isocyanate groups exist some or all of the remaining isocyanate groups are preferably endcapped with an amine or alcohol to terminate the foregoing poly(urethane-urea) resin. Examples of suitable amines are monamines and diamines including, but not limited to butylamine, dibutylamine, aminopropylmorpholine, aminoethylpiperazine,
- 30 dimethylaminopropylamine, di(isopropanol)amine, aminoethoxyethanol, aminoundecanoic acid, ethanolamine, dimethanolamine, 4-aminophenol,

isophoronediamine, dimer diamine, oleyl amine, hydrazine, Jeffamine brand mono or bis (aminopropyl) polypropyleneoxides. Examples of suitable alcohols include, but are not limited to, 1-propanol, 2-propanol, 1-butanol, 2-butanol, neopentyl alcohol, ethanol, oleyl alcohol, 12-hydroxystearic acid, N-(hydroxyethyl)stearamide,
5 ethoxylated nonylphenol, propoxylated nonylphenol, glycolic acid, or 6-hydroxycaproic acid.

The endcapping reaction of any remaining free isocyanate groups is carried out under conditions which are well known to those skilled in the art.

Preferably, this reaction is carried out in the presence of a solvent or in a component
10 of the solvent system ultimately used in the final composition formulated from the ink resin as described above. The total amount of solvent utilized to endcap the free isocyanate groups generally ranges from 0 to 90 percent by weight, preferably ranges from 25 to 75 percent by weight.

The temperature of the endcapping reaction generally ranges from 0 to
15 100°C, and preferably ranges from 25 to 75°C. The time of the endcapping reaction generally ranges from a period of from 0.1 to 6 hours, and preferably from 0.25 to 1 hours. The NCO- equivalent ratio of the chain-extended resin to amine or alcohol generally ranges from 5:1 to 1:5, and preferably ranges from 1:2 to 2:1.

A particularly preferred polyurethane resin prepared as described above
20 is one wherein Z is an isophorone group, R is a C₄ hydrocarbon group, R' is an aminopropylmorpholine radical, X is the residue of isophorone diamine, n is 20, x is 6, and y is 1.75.

Subsequent to forming the resin, some or all of the solvent used as a reaction medium can be removed, e.g., by distillation. Advantageously, the
25 polyurethane resin described herein is soluble in solvents such as alcohol to provide a clear solution. To provide a useful solution of the resin, an alcohol solvent can be added to reach a final dilution of 10 to 90 percent by weight solids, and preferably from 20 to 60 percent by weight solids, and more preferably 30 to 45 percent by weight solids at a temperature of about 20°C. Examples of suitable alcohol solvents
30 include, but are not limited to, aliphatic alcohols, preferably short chain aliphatic alcohols having from 1 to 8 carbon atoms, and more preferably short chain aliphatic

alcohols having from 1 to 4 carbon atoms, e.g., methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, pentanol, hexanol, 2-ethyl hexanol and octanol. Typically, the ratio of alkyl acetate to alcohol solvent ranges from about 1:10 to about 10:1 by weight in the resin solution as supplied for making printing inks. In the final ink
5 composition, flexographic printing inks require at least 80% alcohol solvent to prevent swelling of the flexible printing plates that are based on either rubber or photopolymer.

The resulting clear solution of polyurethane resin in solvent can be used directly, without other additives, as a binder for packaging inks. Other chemicals
10 can be added to the clear polyurethane solution to formulate for a particular application, e.g., use of fillers, thickeners, other co-resins, waxes, etc. In a particularly useful application, the foregoing polyurethane solution can be combined with a pigment to form a printing ink composition. One common technique is expected to use a pigment dispersion in nitrocellulose and solvent that is modified
15 with the polyurethane resins from this invention. Such inks are expected to be suitable for surface printing and laminations.

The printing inks, in general, contain three main components: 1) a pigment which imparts a color to the printing ink, 2) a binder which efficiently disperses the pigment and provides gloss, chemical resistance, toughness, etc. to the
20 printed ink, and 3) a solvent which provides a medium to disperse/dissolve the pigment and binder. In addition to the three main components, the printing ink can also contain other minor additives such as fillers, surfactants, wax and the like to suit a variety of printing needs.

The generic term pigment is specifically used in this specification in
25 that it is intended to refer to both pigments and dyes which impart a distinct color to the printing ink composition. The purpose of any pigment is to provide contrast between the color of a printable substrate and the color of ink in order to provide a visually identifiable indicia on the substrate.

The pigment may be any of those which are typically used in
30 flexographic inks such as monoazo yellows (e.g. CI Pigment Yellows 3, 5, 98); diarylide yellows (e.g. CI Pigment Yellows 12, 13, 14); Pyrazolone Orange,

Permanent Red 2G, Lithol Rubine 4B, Rubine 2B, Red Lake C, Lithol Red, Permanent Red R, Phthalocyanine Green, Phthalocyanine Blue, Permanent Violet, titanium dioxide, carbon black, etc. The pigment is employed in amounts of from 10 to 45 percent by weight, based on the weight of the ink composition.

5 The pigment is combined with the binder resin solution by any convenient method. For example, the pigment can be added to the binder resin solution and, at a properly adjusted viscosity, dispersed therein with ball mill, sand mill, horizontal media mill, high-shear fluid flow mill, Cowles Dissolver®, Kady Mill®, or the like.

10 The viscosity and printing characteristics of the printing ink composition may be modified further by addition of conventional additives such as, plasticizers, sequestered wax, surfactants and the like to suit the particular printing needs.

 The printing processes most advantageously used with the foregoing
15 printing ink are the flexographic and/or gravure printing processes. One characteristic of such printing processes, is that the printing ink composition is applied to a surface of a printable substrate by a hydrophilic cylindrical transfer roll. Printing processes are described, e.g., by T. Sulzberg et al., "Printing Ink Vehicles", *Encyclopedia of Polymer Science and Engineering*, Vol. 13, pp. 368-398 (John Wiley & Sons, Inc.,
20 N.Y., N.Y. 1988), the contents of which are incorporated by reference herein.

 Accordingly, in another aspect, a method of printing is provided which includes applying the foregoing printing ink composition to a printing surface having minute depressions therein which carry the composition, and contacting the printing surface with a printable substrate. This method may be a letterpress printing method
25 (wherein the minute depressions on the printing surface define raised portions of the surface which carry the composition to the substrate, e.g., flexography) or a gravure printing method (wherein the depressions carry the composition to the substrate).

 In flexographic printing in particular, the printing ink composition is applied to a flexible plate mounted on a plate cylinder. The flexible plate is then
30 contacted with a printable substrate by rotation of the plate cylinder. In preferred embodiments, the printing ink composition is applied to the flexible plate with a

cylindrical transfer roll which is rotated to successively take up and then apply successive portions of the composition.

The laminates may contain laminae (layers of substrates) of a wide variety of flexible materials. Thus, suitable laminae include films of polyethylene and polypropylene generally treated for adhesion promotion; also polyester such as polyethylene terephthalate, cellophane and polyamide which may or may not be coated with PVDC for improved barrier properties. Preferably, dissimilar laminae are used where films, for example, of corona treated polypropylene or polyethylene are bonded to polyester, polyamide or PVDC coated cellophane or PVDC coated polyester, or paper. Also contemplated are laminates prepared with woven and non-woven fabrics where the fibers are of cotton, polyester, polyolefin, polyamide, polyimide and the like; metallic foils such as aluminum foil; metallized films; paper and paperboard; and cellular flexible sheet material such as polyethylene foam, polyurethane foam and sponge and foam rubber.

In general, at least one of the laminae will be translucent to visible light and, more typically, transparent. Such translucency or transparency will allow the colorant to present a hue and/or resolvable image through that substrate. The other laminate may also be translucent or transparent, but need not be, for example, when an opaque inner liner is desired.

In the preferred embodiment wherein one of the laminae is a printed surface, any of the conventionally used solvent-borne or aqueous adhesives may be employed in the printing process. Adhesives are discussed in "Adhesive Compositions", *Encyclopedia of Polymer Science and Engineering*, Vol. 1, pp. 547-577 (John Wiley & Sons, Inc. N.Y., N.Y., 1985), the disclosure of which is incorporated by reference herein. As a solvent-borne adhesive, a moisture curable polyurethane in a polar organic solvent is typically used. As an aqueous adhesive, an aqueous emulsion of a flexible adhesive polymer is typically used.

In forming the laminates, conventional techniques known per se are employed to apply the adhesive to the film substrate. Thus, these adhesives may be applied by use of an extrusion process or any mechanical coating process such as air knife, trailing blade, knife coater, reverse roll or gravure coating technique. Most

commonly, the adhesive is coated over the ink on the substrate and allowed to dry. A second substrate is then applied to the adhesive layer under conditions of elevated temperature which activate the adhesive while in contact with the substrate, for example, a corona treated polyethylene or polypropylene film or other lamina.

5 The following examples are meant to illustrate but not to limit the invention.

, 1286 Example 1 *in PP NCO 1000 = 1.5*

180.01 Grams of Terathane 1400 (DuPont product) and 0.07 grams of dibutyltindilaurate were charged to a reaction vessel under nitrogen and heated to 60°C. Over 0.5 hour, *, 1935* 43.11 grams of isophorone diisocyanate was added to the Terathane solution followed by 99.88 grams n-propylacetate. The temperature was increased to 85°C and held for 2 hours. After cooling the reaction to 35°C and adding an additional 48.92 grams propylacetate to the vessel, a solution of *, 6451* 7.71 grams isophorone *, 171* diamine, 4.06 grams diethanol amine in 102.03 grams 1-propanol was added from an addition funnel over 10 minutes. The mixture was held at 45°C for 30 minutes before adding 297.90 grams 1-propanol. After addition of the alcohol, the temperature was held at 85°C for 1 hour. The resulting resin had a molecular weight of 35,200.

20 Example 2

79.09 Grams of Terathane 1000, 100.88 grams of Terathane 2000 (DuPont products) and 0.08 grams of dibutyltindilaurate were charged to a reaction vessel under nitrogen and heated to 60°C. Over 0.5 hour, 42.95 grams of isophorone diisocyanate was added to the Terathane solution followed by 106.56 grams n-propylacetate. The temperature was increased to 85°C and held for 2 hours. After cooling the reaction to 35°C and adding an additional 124.36 grams propylacetate to the vessel, a solution of 4.72 grams isophorone diamine, 3.21 grams diethanol amine in 91.83 grams propylacetate was added from an addition funnel over 10 minutes. The mixture was held at 45°C for 15 minutes before adding 216.07 grams 1-propanol. After addition of the alcohol, the temperature was held at 85°C for 1 hour. The resulting resin had a molecular weight of 39,600.

of diamine
NH₂/NCO = 1.7

, 3866
, 2572
, 1294

, 1294 NCO
, 0902

Example 3

39.85 Grams of isophorone diisocyanate, 59.5 grams ethylacetate, and 0.12 grams of dibutyltindilaurate were charged to a reaction vessel under nitrogen and heated to 65°C. Over 0.5 hour, 253.48 grams of Terathane 2000 (DuPont product) was added to the isocyanate solution followed by 65.0 grams ethylacetate. The temperature was increased to 85°C and held for 2 hours. After cooling the reaction to 50°C, a solution of 5.79 grams isophorone diamine and 75.80 grams ethylacetate was added from an addition funnel over 45 minutes. The mixture was held at 55°C for 30 minutes before adding 5.38 grams diethanol amine in 15.91 grams propylacetate. After holding at 55°C for 20 minutes added 348.62 grams 1-propanol. After addition of the alcohol, the temperature was held at 75°C for 1 hour. The resulting resin had a molecular weight of 66,500.

Example 4

185.75 Grams of Terathane 1400 (DuPont product), 58.27 grams propylacetate, and 0.12 grams of dibutyltindilaurate were charged to a reaction vessel under nitrogen and heated to 60°C. Over 0.5 hour, 44.50 grams of isophorone diisocyanate was added to the Terathane solution followed by 99.88 grams n-propylacetate. The temperature was increased to 85°C and held for 2.75 hours. After cooling the reaction to 35°C and adding an additional 151.71 grams propylacetate to the vessel, a solution of 8.31 grams isophorone diamine in 116.24 grams propylacetate was added from an addition funnel over 30 minutes. The mixture was held at 50°C for 30 minutes before adding 6.57 grams diethanol amine and 220.68 grams 1-propanol. After addition of the alcohol, the temperature was held at 85°C for 1 hour. The resulting resin had a molecular weight of 35,200.

Example 5

200.10 Grams of Terathane 1400 (DuPont product) and 0.19 grams of dibutyltindilaurate were charged to a reaction vessel under nitrogen and heated to 65°C. Over 0.5 hour, 44.50 grams of isophorone diisocyanate was added to

the Terathane solution followed by 205.77 grams n-propylacetate. The temperature was increased to 85°C and held for 2.25 hours. After cooling the reaction to 35°C and adding an additional 223.3 grams propylacetate to the vessel, a solution of 4.15 grams isophorone diamine and 3.67 grams diethanol amine in 90.40 grams propylacetate was added from an addition funnel over 30 minutes. The solution was heated to reflux and 235.67 grams of distillate removed. The mixture was held at 90°C while adding 142.0 grams 1-propanol. The resulting resin had a molecular weight of 55,100.

Example 6

190.90 Grams of Terathane 1400 (DuPont product) and 0.18 grams of dibutyltindilaurate were charged to a reaction vessel under nitrogen and heated to 65°C. Over 0.5 hour, 40.68 grams of isophorone diisocyanate was added to the Terathane solution followed by 207.87 grams n-propylacetate. The temperature was increased to 85°C and held for 2.25 hours. After cooling the reaction to 35°C and adding an additional 89.02 grams propylacetate to the vessel, a solution of 4.07 grams isophorone diamine and 3.41 grams diethanol amine in 82.73 grams propylacetate was added from an addition funnel over 30 minutes. The solution was heated to reflux and 238.92 grams of distillate removed. The mixture was held at 80°C while adding 299.56 grams 1-propanol. The resulting resin had a molecular weight of 37,400.

Example 7

35.74 Grams of isophorone diisocyanate and 0.09 grams of dibutyltindilaurate in 145.62 grams propylacetate were charged to a reaction vessel under nitrogen and heated to 60°C. Over 1 hour, 166.40 grams of Terathane 1400 (DuPont product) was added to the isocyanate solution followed by another 36.0 grams n-propylacetate. The temperature was increased to 85°C and held for 2.25 hours. After cooling the reaction to 35°C, a solution of 3.07 grams isophorone diamine in 120.0 grams propylacetate was added from an addition funnel over 15 minutes. A solution of 2.85 grams diethanolamine in 85.84 grams propylacetate was added over 15 minutes. The solution was heated to reflux and 297.16 grams of distillate removed. The mixture was held at 90°C while adding 226.05 grams 1-

propanol and 69.55 grams propylacetate. The resulting resin had a molecular weight of 33,200.

Example 8

5 180.41 Grams of Terathane 1400 (DuPont product) and 0.12 grams of dibutyltindilaurate in 100.54 grams propylacetate were charged to a reaction vessel under nitrogen and heated to 65°C. Over 1 hour, 47.32 grams of 1,3 bis(isocyanato-1-methylethylbenzene) (also known as TMDI or tetramethylxylene diisocyanate) was added to the Terathane solution. The temperature was increased to 85°C and held for
10 3 hours. After cooling the reaction to 45°C and adding an additional 126.60 grams propylacetate to the vessel, a solution of 7.44 grams isophorone diamine and 3.35 grams diethanolamine in 24.48 grams propylacetate was added from an addition funnel over 30 minutes. The resin solution heated to 85°C while adding 203.76 grams 1-propanol. The resulting resin had a molecular weight of 89,200.

Example 9

32.05 Grams of isophorone diisocyanate and 0.09 grams of
dibutyltindilaurate in 100.46 grams propylacetate were charged to a reaction vessel under nitrogen and heated to 60°C. Over 1 hour, 147.98 grams of Terathane 1400
20 (DuPont product) was added to the isocyanate solution followed by another 60.89 grams n-propylacetate. The temperature was increased to 85°C and held for 2.25 hours. After cooling the reaction to 35°C, a solution of 1.80 grams isophorone diamine in 107.31 grams propylacetate was added from an addition funnel over 15 minutes. A solution of 2.64 grams diethanolamine in 83.68 grams propylacetate was
25 added over 15 minutes. The solution was heated to reflux and 250.76 grams of distillate removed. The mixture was held at 90°C while adding 204.02 grams 1-propanol and 28.79 grams propylacetate. The resulting resin had a molecular weight of 27,900.

Example 10

250.03 Grams of Terathane 1400 (DuPont product) and 0.24 grams of dibutyltindilaurate were charged to a reaction vessel under nitrogen and heated to 65°C. Over 0.5 hour, 59.55 grams of isophorone diisocyanate in 71.31 grams propylacetate was added to the Terathane solution. The temperature was increased to 85°C and held for 2 hours. After cooling the reaction to 35°C and adding an additional 94.45 grams propylacetate to the vessel, a solution of 11.40 grams isophorone diamine in 48.22 grams propylacetate was added from an addition funnel over 30 minutes. A solution of 4.71 grams diethanolamine in 94.45 grams 2-propanol was added to the reaction over 10 minutes. The solution was heated to 65°C while adding 271.20 grams 2-propanol, warmed to 85°C and held for 1 hour. The resulting resin had a molecular weight of 55,600.

Example 11

59.79 Grams of isophorone diisocyanate and 0.24 grams of dibutyltindilaurate in 70.51 grams propylacetate were charged to a reaction vessel under nitrogen and heated to 60°C. Over 1 hour, 250.91 grams of Terathane 1400 (DuPont product) was added to the isocyanate solution. The temperature was increased to 85°C and held for 2 hours. After cooling the reaction to 35°C and adding an additional 94.65 grams propylacetate to the vessel, a solution of 11.44 grams isophorone diamine in 49.60 grams propylacetate was added from an addition funnel over 15 minutes. A solution of 4.75 grams diethanolamine in 99.04 grams 2-propanol was added over 15 minutes. The solution was heated to 55°C while adding 270.75 grams 2-propanol. The resin solution was then heated to 85°C and held for 1 hour. The resulting resin had a molecular weight of 68,100.

Example 12

31.91 Grams of isophorone diisocyanate, 13.69 grams of Vestanat TMDI from Crenova (mixed isomers of trimethylhexane 1,6 diisocyanate) and 0.16 grams of dibutyltindilaurate in 24.94 grams propylacetate were charged to a reaction vessel under nitrogen and heated to 60°C. Over 1 hour, 200.32 grams of Terathane

1400 (DuPont product) was added to the isocyanate solution followed by an additional 31.23 grams propylacetate. The temperature was increased to 85°C and held for 2 hours. After cooling the reaction to 35°C and adding an additional 108.78 grams propylacetate to the vessel, a solution of 3.82 grams isophorone diamine in 81.61 grams propylacetate was added from an addition funnel over 15 minutes. The solution was heated to 60°C while adding 202.18 grams 1-propanol. The resin solution was then heated to 85°C and held for 1 hour. The resulting resin had a molecular weight of 20,480.

10 Example 13

41.83 Grams of isophorone and 0.15 grams of dibutyltindilaurate in 32.52 grams propylacetate were charged to a reaction vessel under nitrogen and heated to 70°C. Over 1 hour, 180.36 grams of Terathane 1400 (DuPont product) was added to the isocyanate solution followed by an additional 26.62 grams propylacetate. The temperature was increased to 85°C and held for 2 hours. After cooling the reaction to 35°C and adding an additional 87.88 grams propylacetate to the vessel, a solution of 3.24 grams piperazine in 73.22 grams propylacetate was added from an addition funnel over 15 minutes. The solution was heated to 60°C while adding 193.22 grams 1-propanol. The resin solution was then heated to 85°C and held for 1 hour. The resulting resin had a molecular weight of 44,500.

Example 14

31.78 Grams of isophorone diisocyanate, 13.73 grams of Vestanat TMDI from Crenova (mixed isomers of trimethylhexane 1,6 diisocyanate) and 0.15 grams of dibutyltin dilaurate in 48.78 grams propylacetate were charged to a reaction vessel under nitrogen and heated to 60°C. Over 1 hour, 200.32 grams of Terathane 1400 (DuPont product) was added to the isocyanate solution followed by an additional 45.51 grams propylacetate. The temperature was increased to 85°C and held for 2 hours. After cooling the reaction to 60°C and adding an additional 44.19 grams propylacetate to the vessel, a solution of 4.71 grams aminoethylpiperazine in 133.87 grams propylacetate was added from an addition funnel over 2 hours. The

solution was held to 60°C while adding 192.34 grams 1-propanol. The resin solution was then heated to 85°C and held for 1 hour. The resulting resin had a molecular weight of 44,200.

5

Example 15

26.96 Grams of isophorone diisocyanate, 11.53 grams of Vestanat TMDI from Crenova (mixed isomers of trimethylhexane 1,6 diisocyanate) and 0.16 grams of dibutyltindilaurate in 58.22 grams propylacetate were charged to a reaction vessel under nitrogen and heated to 60°C. Over 1 hour, a mixture of 115.02 grams of
10 Terathane 1400 (DuPont product) and 38.36 grams Stepanol PD 110-LV from Stepan Corporation (a polyester diol from orthophthalic acid and diethylene glycol) was added to the isocyanate solution followed by an additional 28.53 grams propylacetate. The temperature was increased to 85°C and held for 2 hours. After cooling the reaction to 55°C and adding an additional 104.75 grams propylacetate to
15 the vessel, a solution of 6.62 grams isophorone diamine in 80.25 grams propylacetate was added from an addition funnel over 2 hours. The solution was heated to 60°C while adding 112.51 grams 1-propanol. The resin solution was then heated to 85°C and held for 1 hour. The resulting resin had a molecular weight of 136,000.

20

Example 16

51.60 Grams of isophorone diisocyanate and 0.10 grams of dibutyltindilaurate in 37.36 grams propylacetate were charged to a reaction vessel under nitrogen and heated to 60°C. Over 1 hour, 196.032 grams of Terathane 1400 (DuPont product) was added to the isocyanate solution followed by an additional
25 34.50 grams propylacetate. The temperature was increased to 85°C and held for 2 hours. After cooling the reaction to 60°C, a solution of 7.44 grams isophorone diamine and 5.30 grams aminopropylmorpholine in 245.4 grams propylacetate was added from an addition funnel over 1.5 hours. The solution was heated to 60°C while adding 166.28 grams 1-propanol.

30

Example 17

56.71 Grams of isophorone diisocyanate and 0.13 grams of dibutyltindilaurate in 22.65 grams propylacetate were charged to a reaction vessel under nitrogen and heated to 60°C. Over 1 hour, 169.49 grams of Terathane 1400 (DuPont product) was added to the isocyanate solution. The temperature was increased to 85°C and held for 2 hours. After cooling the reaction to 60°C and adding an additional 105.15 grams propylacetate to the vessel, a solution of 18.15 grams isophorone diamine in 150.51 grams propylacetate was added from an addition funnel over 2 hours. The solution was held to 60°C while adding 3.87 grams dimethylaminopropylamine in 16.0 grams propylacetate over 30 minutes followed by 165.34 grams 1-propanol.

Example 18

138.60 Grams of isophorone diisocyanate, 0.14 grams of dibutyltindilaurate, and 776 grams n-propylacetate were charged to a reaction vessel under nitrogen and heated to 70°C. Over 1 hour, 497.05 grams of Terathane 1400 (DuPont product) was added to the isocyanate solution. The temperature was increased to 85°C and held for 3 hours. After cooling the reaction to 55°C a solution of 43.40 grams isophorone diamine in 84.58 grams propylacetate was added from an addition funnel over 15 minutes. The mixture was held at 55°C for 30 minutes before adding 400.37 grams 1-propanol. After addition of the alcohol, the temperature was raised to 65°C and held for 1 hour. The resulting resin had a molecular weight of 42,500.

Example 19

229.81 Grams of isophorone diisocyanate, 0.11 grams of dibutyltindilaurate, and 593.71 grams n-propylacetate were charged to a reaction vessel under nitrogen and heated to 70°C. Over 1 hour, 1052.37 grams of Terathane 2000 (DuPont product) was added to the warm isocyanate solution. The temperature was increased to 85°C and held for 3 hours. After cooling the reaction to 45°C the vessel contents were pumped via an FMI Lab Pump over 1.5 hours to another vessel

containing 109.03 grams isophorone diamine in 1102.61 grams propylacetate. The mixture was held at 55°C for 30 minutes before adding 887.24 grams 1-propanol. After addition of the alcohol, the temperature was raised to 65°C and held for 1 hour. The polyurethane solution was 35% resin, 42.7% propylacetate, and 22.3% 1-propanol. The resulting resin had a molecular weight of 32,000.

Example 20

100.42 Grams of isophorone diisocyanate, 0.04 grams of dibutyltindilaurate, and 236.95 grams n-propylacetate were charged to a reaction vessel under nitrogen and heated to 70°C. Over 1 hour, 466.95 grams of Terathane 2000 (DuPont product) was added to the warm isocyanate solution. The temperature was increased to 85°C and held for 3 hours. After cooling the reaction to 45°C the vessel contents were pumped via an FMI Lab Pump over 1.5 hours to another vessel containing a solution of 46.80 grams isophorone diamine in 694.31 grams of 2-propanol. After addition of the two solutions, the temperature was raised to 65°C and held for 1 hour. The resulting polyurethane solution was 40% resin, 14.8% propylacetate, and 45.2% 2-propanol. The resin had a molecular weight of 32,700.

Example 21

120.02 Grams of isophorone diisocyanate, 0.06 grams of dibutyltindilaurate, and 216.71 grams n-propylacetate were charged to a reaction vessel under nitrogen and heated to 70°C. Over 1 hour, 154.82 grams of Acclaim 2220N poly(propylene oxide) diol from Lyondell and 227.12 grams of Stepanpol PN-110 (a polyester diol from orthophthalic acid and neopentyl glycol) were added to the warm isocyanate solution. The temperature was increased to 85°C and held for 3 hours. After cooling the reaction to 45°C the vessel contents were pumped via an FMI Lab Pump over 1.5 hours to another vessel containing 45.61 grams isophorone diamine in 431.65 grams propylacetate. The mixture was held at 55°C for 30 minutes before adding 368.48 grams 1-propanol. After addition of the alcohol, the temperature was raised to 65°C and held for 1 hour. The polyurethane solution was

35% resin, 41.4% propylacetate, and 23.6% 1-propanol. The resulting resin had a molecular weight of 14,300.

Example 22

5 83.72 Grams of isophorone diisocyanate, 0.04 grams of dibutyltindilaurate, and 219.04 grams n-propylacetate were charged to a reaction vessel under nitrogen and heated to 70°C. Over 1 hour, 389.31 grams of Terathane 2000 (DuPont product) was added to the warm isocyanate solution. The temperature was increased to 85°C and held for 3 hours. After cooling the reaction to 45°C the
10 vessel contents were pumped via an FMI Lab Pump over 1.5 hours to another vessel containing 42.14 grams isophorone diamine in 406.79 grams propylacetate. The mixture was held at 55°C for 30 minutes before adding 330.89 grams 1-propanol. After addition of the alcohol, the temperature was raised to 65°C and held for 1 hour. The polyurethane solution was 35% resin, 42.5% propylacetate, and 22.5% 1-
15 propanol. The resulting resin had a molecular weight of 31,000.

Example 23

 45.01 Grams of isophorone diisocyanate, 0.11 grams of dibutyltindilaurate, and 85.35 grams n-propylacetate were charged to a reaction vessel
20 under nitrogen and heated to 60°C. Over 1 hour, 188.12 grams of Terathane 1400 (DuPont product) was added to the isocyanate solution. The temperature was increased to 85°C and held for 2.5 hours. After cooling the reaction to 45°C and adding an additional 182.71 grams propylacetate, a solution of 12.27 grams isophorone diamine in 100.05 grams propylacetate was added from an addition funnel
25 over 45 minutes. The mixture was held at 65°C for 30 minutes before adding 7.86 grams of diethanol amine. After half an hour 222.8 grams 1-propanol was added. After addition of the alcohol, the temperature was held at 65°C for 1 hour. The resulting resin had a molecular weight of 83,900.

30

Example 24

180.31 Grams of Terathane 1400 (DuPont product) and 0.09 grams of dibutyltindilaurate were charged to a reaction vessel under nitrogen and heated to 60°C. Over 0.5 hour, 43.15 grams of isophorone diisocyanate was added to the Terathane solution followed by 294.33 grams n-propylacetate. The temperature was increased to 80°C and held for 3 hours. After cooling the reaction to 50°C, a solution of 29.70 grams isophorone diamine in 34.94 grams propylacetate was added from an addition funnel over 1 hour. The mixture was held at 65°C for 30 minutes before adding 12.90 grams of diethanol amine. After half an hour 291.51 grams 1-propanol was added. After addition of the alcohol, the temperature was held at 85°C for 1 hour. The resulting resin had a molecular weight of 43,800.

Preparation of Lamination Ink Compositions

Lamination ink compositions are prepared using the components listed in Table 1 below.

Table 1: General Lamination Ink Composition

WHITE INK COMPOSITIONS	Wt%
polyurethane solution of the examples	40.0
n-propanol	16.0
n-propyl acetate	4.0
Titanium Dioxide pigment	40.0
Total	100.00

To prepare each white ink composition, add 30g of 4mm glass beads then grind 20 minutes on shaker and dilute to 60.0 centipoise with 80/20 solvent blend n-propanol/ethyl acetate.

A film of each white ink composition is cast with a flexographic hand proofer onto clear polyester film or polypropylene film. The adhesive is applied over the ink film for adhesive lamination. Then the polyethylene film is applied on top of the adhesive. For extrusion lamination the polyethylene film is heated to melting temperature and applied with heat and pressure. The results of these experiments are shown in Tables 2-5 below.

Table 2: Green Extrusion Lamination Bond Strength Polyethylene Terephthalate/Polyethylene (PET/PE) (with tape back-up on PET)

Extrusion Laminate*	Average mean bond strength (g/in)**	% Decal***
1	236.1	25
2	118.9	100
3	180.5	75
4	231.5	75
5	18.6	100
6	306.1	75
7	40.2	100
8	128.7	75
9	47.1	100
10	139.2	50
23	45.5	75
24	71.6	90

5 * Extrusion Laminates are identified by the number corresponding to the foregoing polyurethane preparation examples.

**Bond strength measured with the Thwing Albert 225-1 T-peel tester.

***100% Decal is equal to complete ink film transfer upon bond failure. 0% Decal represents no transfer of ink film.

10

Table 3: Adhesive Lamination Bond Strength PET/PE Using Two Part Urethane Adhesive Morton 532 A/B (Morton Chemical/Rohm and Hass)

Adhesive Laminate*	Average mean bond strength (g/in)	% Decal
18	450	100
19	460	100

15 *Adhesive Laminates are identified by the number corresponding to the foregoing polyurethane preparation examples.

20

**Table 4: Max. Extrusion Lamination Bond Strength
polypropylene/polyethylene and polyester/polyethylene**

Extrusion Laminate*	POLYPROPYLENE	POLYESTER
11	150g/in	120g/in
10	220	150
3	250	100

- 5 * Extrusion Laminates are identified by the number corresponding to the foregoing polyurethane preparation examples.

**Table 5: Max. Adhesive Lamination Bond Strength
Polypropylene/Polyethylene and Polyester/Polyethylene Using HSA Two Part
Adhesive Applied With a #8 Meyer Bar**

10

Adhesive Laminate*	POLYPROPYLENE 24 hr aged %decal	POLYESTER 24 hr aged	% Decal
11	>350g/in 90	>350g/in	90
10	>350g/in 90	>350g/in	90
3	>350g/in 90	>350g/in	50

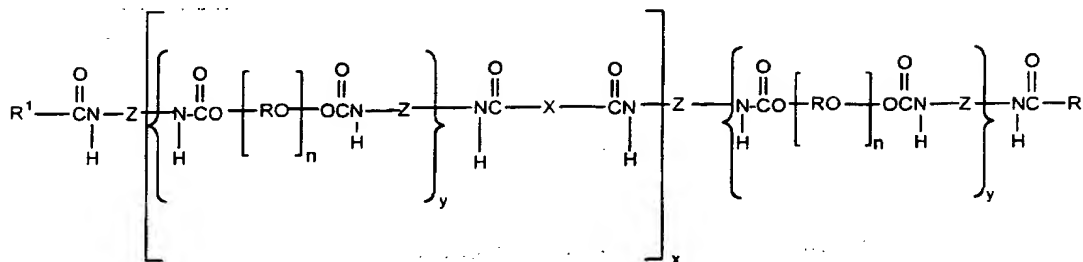
*Adhesive Laminates are identified by the number corresponding to the foregoing polyurethane preparation examples.

- 15 It will be understood that various modifications may be made to the embodiments disclosed herein. Therefore, the above description should not be construed as limiting, but merely as exemplifications of the preferred embodiments. Those skilled in the art will envision other modifications within the scope and spirit of the claims appended hereto.

20

WHAT IS CLAIMED:

1. A polyurethane resin of the general formula:



5

wherein Z is an aliphatic, cycloaliphatic, aromatic, or alkylaromatic group, R is a C₂ to C₈ straight chain or branched hydrocarbon group, the reaction product of a C₂ to C₃₆ diol with a C₂ to C₃₆ diacid equivalent, or mixtures thereof, R¹ is an amine or alcohol radical, X is the residue of a diamine, n is a number from 1 to 200, x is a number from 1 to 50, and y is a number from 1 to 30, the polyurethane resin being soluble in a solvent containing an aliphatic alcohol to a level of at least 10 percent by weight solids.

15

2. The polyurethane resin of claim 1, wherein the resin is soluble in the alcohol to a level of about 20 to 60 percent by weight solids.

20

3. The polyurethane resin of claim 2, wherein the resin is soluble in the alcohol to a level of about 30 to 45 percent by weight solids.

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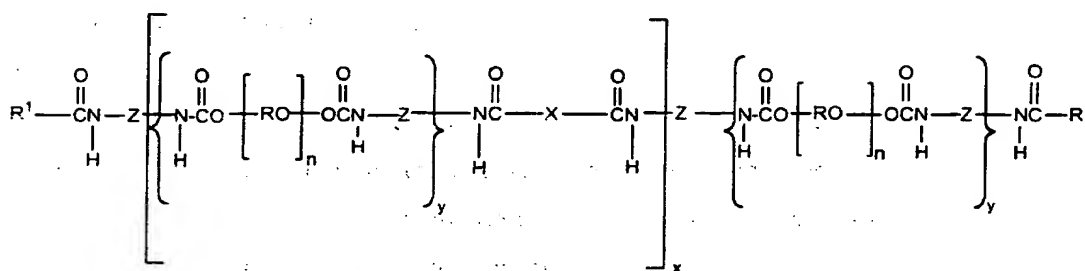
4. The polyurethane resin of claim 1, wherein R is a C₄ straight chain hydrocarbon group.

25

5. The polyurethane resin of claim 1, wherein the diamine residue is an isophorone diamine residue.

5 6. The polyurethane resin of claim 1, wherein the R¹ radical is an aminopropylmorpholine radical.

7. A polyurethane resin of the general formula:



wherein Z is an isophorone group, R is a C₄ straight chain hydrocarbon group R¹ is an aminopropylmorpholine radical, X is the residue of an isophorone diamine, n is a number from 1 to 200, x is a number from 1 to 50, and y is a number from 1 to 30, the polyurethane resin being soluble in a solvent containing an aliphatic alcohol to a level of at least 10 percent by weight solids.

8. The polyurethane resin of claim 7, the resin being soluble in the alcohol to a level of about 20 to 60 percent by weight solids.

9. The polyurethane resin of claim 8, the resin being soluble in the alcohol to a level of about 30 to 45 percent by weight solids.

10. A clear solution comprising the polyurethane resin of claim 1 and a solvent, wherein the solvent comprises an aliphatic alcohol.

11. The clear solution of claim 10, wherein the solvent further
5 comprises an alkyl acetate.

12. The clear solution of claim 11, wherein the aliphatic alcohol is 1-propanol and the alkyl acetate is propyl acetate.

13. A method of preparing a polyurethane resin which comprises:
a) reacting an excess of an aliphatic, cycloaliphatic, aromatic, or
alkylaromatic diisocyanate with a polymeric diol selected from the group consisting
of one or more polyether diols, one or more polyester diols and mixtures thereof to
form an isocyanate-terminated prepolymer;
15 b) reacting the isocyanate-terminated prepolymer with a diamine; and
c) optionally reacting the compound produced by step (b) with an
amine or alcohol to form the polyurethane resin, the resin being soluble in a solvent
containing an aliphatic alcohol to a level of at least 10 percent by weight solids.

14. The method of claim 13, the polyurethane resin being soluble in
20 the alcohol to a level of about 20 to 60 percent by weight solids.

15. The method of claim 14, the polyurethane resin being soluble in
the alcohol to a level of about 30 to 45 percent by weight solids.

16. The method of claim 13 wherein step (a) is conducted in the
25 presence of a catalyst.

17. The method of claim 16 wherein the catalyst is selected from the
30 group consisting of stannous octylate, stannous oxalate, dibutyltin dilaurate and
triethylamine.

18. The method of claim 17 wherein the catalyst is dibutyltin dilaurate.

5

19. The method of claim 13 wherein the polyether diol is poly(tetramethylene ether) glycol.

20. The method of claim 19 wherein the poly(tetramethylene ether) glycol has a weight average molecular weight of from about 500 to about 10,000.

10

21. The method of claim 13 wherein the diamine is isophorone diamine.

15

22. The method of claim 13 wherein step (a) is performed in the presence of a solvent.

23. The method of claim 22 wherein the solvent is an alkyl acetate selected from the group consisting of methyl acetate, ethyl acetate and propyl acetate.

20

24. The method of claim 23 wherein the solvent is propyl acetate.

25. A polyurethane resin produced by a method comprising:

a) reacting an excess of an aliphatic, cycloaliphatic, aromatic, or alkylaromatic diisocyanate with a polymeric diol selected from the group consisting of one or more polyether diols, one or more polyester diols and mixtures thereof to form an isocyanate-terminated prepolymer;

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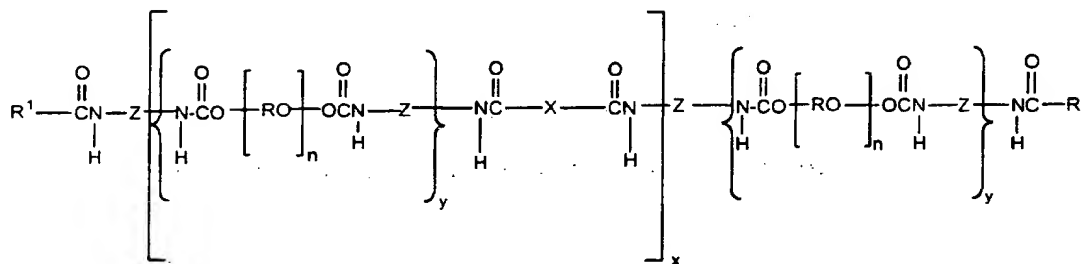
b) reacting the isocyanate-terminated prepolymer with a diamine; and

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c) optionally reacting the compound produced by step (b) with an amine or alcohol, to form the polyurethane resin, the resin being

soluble in a solvent containing an aliphatic alcohol to a level of at least 10 percent by weight solids.

26. An ink composition comprising a polyurethane resin of the general
5 formula:



wherein Z is an aliphatic, cycloaliphatic, aromatic, or alkylaromatic group, R is a C₂ to C₈ straight chain or branched hydrocarbon group, the reaction product of C₂ to C₃₆ diol with a C₂ to C₃₆ diacid equivalent, or mixtures thereof, R' is an amine or alcohol radical, X is the residue of a diamine, n is a number from 1 to 200, x is a number from 1 to 50, and y is a number from 1 to 30, a solvent comprising an aliphatic alcohol, and a pigment, wherein the polyurethane resin is soluble in the alcohol to a level of at least 10 percent by weight solids.

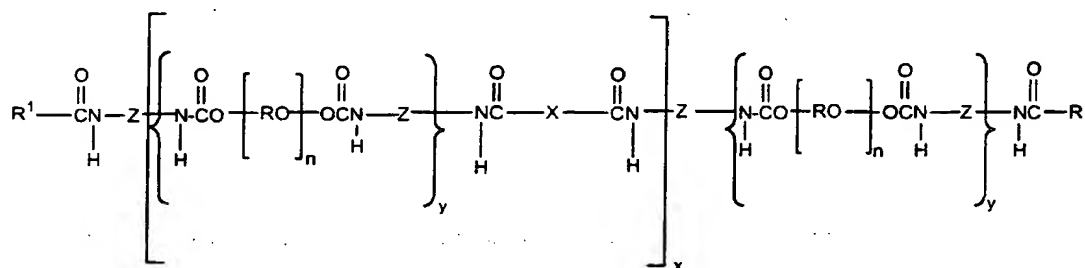
27. The ink composition of claim 26, the resin being soluble in the alcohol to a level of about 20 to 60 percent by weight solids.

20 28. The ink composition of claim 27, the resin being soluble in the alcohol to a level of about 30 to 45 weight percent solids.

29. The ink composition of claim 26, wherein the solvent further comprises an alkyl acetate.

30. The ink composition of claim 29, wherein the aliphatic alcohol is 1-propanol and the alkyl acetate is propyl acetate.

31. A method of preparing an ink composition comprising:
 5 providing a solution of a polyurethane resin of the general formula:



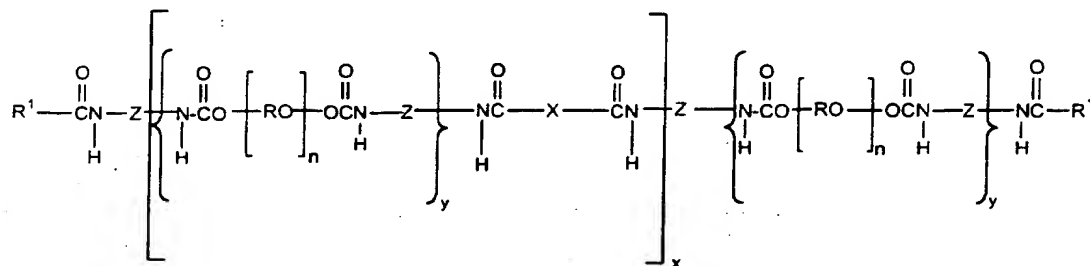
10 wherein Z is an aliphatic, cycloaliphatic, aromatic, or alkylaromatic group, R is a C₂ to C₈ straight chain or branched hydrocarbon group, the reaction product of C₂ to C₃₆ diol with a C₂ to C₃₆ diacid equivalent, or mixtures thereof, R¹ is an amine or alcohol radical, X is the residue of a diamine, n is a number from 1 to 200, x is a number from 1 to 50, and y is a number from 1 to 30, in a solvent comprising an aliphatic alcohol
 15 and combining the solution with a pigment, the polyurethane resin being soluble in the alcohol to a level of at least 10 percent by weight solids.

32. The method of claim 31, wherein the polyurethane resin is soluble in the alcohol to a level of about 20 to 60 percent by weight solids.

33. The method of claim 32, wherein the polyurethane resin is soluble in the alcohol to a level of about 30 to 45 percent by weight solids.

34. The method of claim 33 wherein the solvent further comprises an
 25 alkyl acetate.

36. A method of preparing a laminate which comprises:
coating a surface of a first substrate with a printing ink composition including a pigment, a solvent comprising an aliphatic alcohol and a polyurethane resin of the general formula:

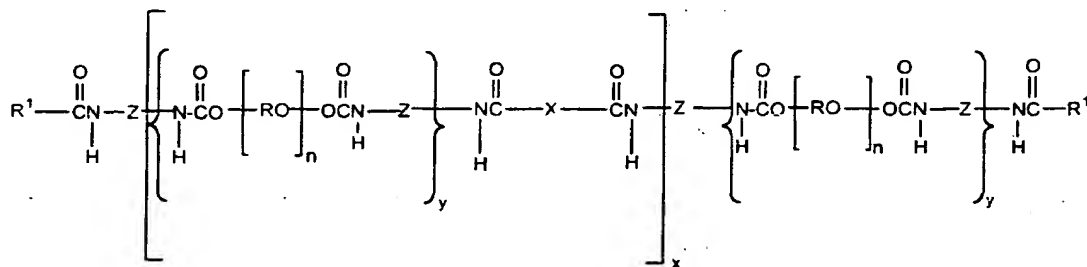


wherein Z is an aliphatic, cycloaliphatic, aromatic, or alkylaromatic group, R is a C₂ to C₈ straight chain or branched hydrocarbon group, the reaction product of a C₂ to C₃₆ diol with a C₂ to C₃₆ diacid equivalent, or mixtures thereof, R¹ is an amine or alcohol radical, X is the residue of a diamine, n is a number from 1 to 200, x is a number from 1 to 50, and y is a number from 1 to 30, wherein the polyurethane resin is soluble in the alcohol to a level of at least 10 percent by weight solids;
removing the solvent to provide a film on the surface of the first substrate; and
contacting a second substrate with the film under conditions of elevated temperature whereby the substrates adhere to form a laminate.

37. The method of claim 36 wherein the solvent further comprises an alkyl acetate.

38. The method of claim 37 wherein the alcohol is 1-propanol and the alkyl acetate is propyl acetate.

35. A laminate comprising a first substrate having an ink composition applied to a surface thereof, the ink composition comprising a pigment and a polyurethane resin of the general formula:



wherein Z is an aliphatic, cycloaliphatic, aromatic, or alkylaromatic group, R is a C₂ to C₈ straight chain or branched hydrocarbon group, the reaction product of a C₂ to C₃₆ diol with a C₂ to C₃₆ diacid equivalent, or mixtures thereof, R' is an amine or alcohol radical, X is the residue of a diamine, n is a number from 1 to 200, x is a number from 1 to 50, and y is a number from 1 to 30, the polyurethane resin being soluble in a solvent containing an aliphatic alcohol to a level of at least 10 percent by weight solids and a second substrate in contact with the ink composition, wherein at least a portion of the ink composition secures at least a portion of the first and second substrates in a fixed relation.

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 00/22471

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/10 C08G18/12 C08G18/72 C08G18/40 C08G18/48
C09D11/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP G 604 890 A (SAKATA INX CORP) 6 July 1994 (1994-07-06) page 2, line 49 -page 5, line 37 example 2; table 1 page 7, line 6 - line 42	1,5,7, 10,13, 21,25, 26,31
X	DATABASE WPI Section Ch, Week 199339 Derwent Publications Ltd., London, GB; Class A25, AN 1993-309340 XP002153575 & JP 05 222333 A (ARAKAWA CHEM IND LTD), 31 August 1993 (1993-08-31) abstract ----- -/--	1-3,5, 10, 13-15, 21, 25-28, 31-33

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

22 November 2000

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01/12/2000

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	<p>DATABASE WPI Section Ch, Week 198945 Derwent Publications Ltd., London, GB; Class A25, AN 1989-327740 XP002153577 & JP 01 242674 A (KURARAY CO LTD), 27 September 1989 (1989-09-27) abstract</p> <p style="text-align: center;">-----</p>	<p>1, 4, 5, 7, 13, 19, 26</p>

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INTERNATIONAL SEARCH REPORT

information on patent family members

Inter: nal Application No

PCT/US 00/22471

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